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(21) International Application Number: PCT/EP96/00136 (22) International Filing Date: 15 January 1996 (15.01.96) (30) Priority Data: MI95A000083 20 January 1995 (20.01.95) IT (71) Applicant (for all designated States except US): COMMER S.P.A. [IT/IT]; Zona Industriale Contrada Ficocelle, I-84061 Ogliastro Cilento (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): SIANO, Dante [IT/IT]; Via Treviso, 10, I-20093 Cologno Monzese (IT). MASCIA, Francesco [IT/IT]; Via Cavour, 1, I-22070 Guanzate (IT). (74) Agent: GISLON, Gabriele; Marietti e Gislou S.r.l., Via Larga, 16, I-20122 Milano (IT).	(81) Designated States: BR, CA, JP, KR, MX, SG, TR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: GRAFTED PROPYLENE HOMO AND COPOLYMERS AND A PROCESS FOR THEIR PRODUCTION**(57) Abstract**

A resin material provided with softness and good rheological properties, suitable for injection molding, and showing no tackiness is obtained by grafting propylene homo and copolymers with grafting units selected from polyalkenilenes (1 to 30 % by weight) and EP(D)M polymers (5 to 65 % by weight), or mixtures thereof, and optionally with vinyl polybutadiene grafting units (0.01 to 10 % by weight).

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- 1 -

"GRAFTED PROPYLENE HOMO AND COPOLYMERS AND A PROCESS FOR THEIR PRODUCTION"

FIELD OF THE INVENTION

The present invention relates to grafted propylene homo and co-polymers and to a process for their preparation. The grafting units are selected from 1,2 polydienes, polyalkenylenes and amorphous elastomers obtained through copolymerization of ethylene-propylene (EPM) or ethylene-propylene with a not conjugated diene monomer (EPDM)

Particular, the present invention concerns a resin suitable to be used as synthetic leather for articles such as, for instance, interior car door panels.

BACKGROUND OF THE INVENTION

The production of interior door panels, dashboard elements, interior trims, consoles and similar parts was usually carried out by coupling a layer of synthetic leather to a supporting element. The two main coupling methods are by glueing the synthetic leather to a rigid support or by pressing and shaping said synthetic leather in a mold together with a heated thermoplastic supporting element.

Recently, the applicant developed a process to produce panels or similar elements by means of co-injection of an outer skin (that represents the synthetic leather) and an inner support layer that gives to the final part the

- 2 -

requested rigidity.

One of the problems to be solved using such technology resides in the physical properties of the skin material. The skin material has to join a pleasant-touch (softness) characteristic with a easy-flow behaviour (for injection molding). Polymers having either pleasant-touch or easy-flow behaviour are well known. Polymers with a good pleasant-touch are, e.g., thermoplastic elastomers (TPE) and the polyolefin thermoplastic elastomers (PTE) that are EP or EPDM blends polyolefin based, whose properties are quite similar to a rubber, or the new TPO (thermoplastic polyolefin) materials which behave themselves as a thermoplastic elastomer.

Unfortunately, whilst these materials are provided with the pleasant touch characteristic, they are lacking the required easy-flow behaviour; thus, they can not be used in an injection molding process.

The easy flow behaviour is usually achieved via reactive degradation, i.e. a process that reduces the molecular weight (molecular chain length) of the polymer. It is known to carry out selective degradation of propylene homo and co-polymers by means of peroxide or non-peroxide radical initiators.

The use of peroxide radical initiators such as dicumyl peroxide (DCUP), di(tert-butyl) peroxide or of non-

- 3 -

peroxide radical initiators such as 2,3-dimethyl-2,3-diphenylethane or 3,4-dimethyl-3,4-diphenylhexane in a concentration between 0.1 to 1.0 by weight, results in an improvement of the rheological properties (easy-flow) of the propylene polymers. The drawbacks of this method are that the mechanical properties (modulus and impact strength) of the polymers are lowered and that molecules having low weight molecular chains are by-produced. These products have a low melting point and, at low temperature, they become viscous liquids that migrate towards the surface of the molded piece, making it stacky and not suitable to be used.

It is known to modify (grafting) crystalline propylene polymers by treating them at temperatures within the range of 150° to 300°C with alfa-olefin polymers and copolymers, for example 1-butene, in the presence of a peroxide radical initiators (European patent 261.786) or of non-peroxide radical initiators (European patent 542.253). In both cases it is not achieved the reorganisation of the low weight polymeric chains, hence there is not any reduction of the final piece tackiness even at quite low temperature (<60°C).

Polyalkenylenes grafted on propylene are known as well (Plastic, Rubber and Composite Processing and Application 18, Pg 47-58, 1992 and European Patent EP 642.622). In

- 4 -

this case the obtained resins show, in spite of a tackiness reduction, a substantial melt fluidity reduction such as to preclude their processability in injection and co-injection molding.

OBJECT OF THE INVENTION

The aim of the present invention is to solve the above mentioned problems by providing propylene polymers endowed with the properties requested, and a process for their preparation.

SUMMARY OF THE INVENTION

Said object is obtained by means of the present invention that relates to homopolymers and copolymers of propylene according to claim 1.

The invention also relates to a process for preparing said (co)polymers, according to claim 8.

The invention further relates to the use of the above mentioned polymers for producing interior car door panels or other interior elements, according to claim 15.

According to a preferred embodiment, the propylene (co)polymers comprise, as grafting units, 5 to 65% of grafted amorphous elastomer obtained through copolymerization of ethylene-propylene (EMP), or ethylene-propylene diene monomer (EPDM). Both EPM and EPDM Polymers can be extended with naphtene/paraffin oil.

According to another embodiment, the propylene

- 5 -

(co)polymers comprise also from 0.1 to 5% by weight of vinyl polybutadiene as grafting units.

According to a further embodiment of the invention, the (co)polymers are obtained by thermal degradation with the presence of peroxide initiators.

The (co)polymers according to the present invention solve the technical problem above mentioned : thanks to their fluidity they are suitable for injection or co-injection molding process, and the final item thus obtained shows no tackiness. The invention (co)polymers are also suitable for production of synthetic leather or other items having a good softness, i.e. the pleasant-touch characteristic, with no tackiness. A synthetic leather so obtained could be used to produce car trim panels according to the glueing or hot pressing methods above referred to.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As above mentioned, propylene homo and copolymers are grafted by using grafting units selected from polyalkenylenes, EPM and EPDM polymers, or mixtures thereof, the amount of polyalkenylenes being within the range from 1 to 30% by weight and the amount of EPM and/or EPDM polymers being within the range from 5 to 65% by weight of the total composition.

In a preferred embodiment, also vinylbutadienes, i.e. α -olefins polymers, are added as grafting units to those

- 6 -

mentioned above, the amount of vinylpolybutadiene being within the range from 0.01 to 10% by weight.

The preferred starting polymers are propylene polymers, however other starting polymers can be used. The polymer object of the invention can be prepared by means of reactive transformation (degradation) for example in a extruder or directly during the injection or co-injection molding.

The material fluidity can be kept steady, increased or reduced and in the meantime its softness will be improved making it, in terms of superficial hardness, similar to thermoplastic elastomers.

The process of the invention consists in mixing at a temperature range within 160° to 310°C propylene polymers with polyalkenylenes and/or amorphous ethylene-propylene copolymers and/or ethylene-propylene-diene terpolymers and optionally, but not necessarily, with alfa-olefins polymers in the presence of radical initators.

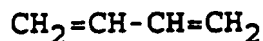
Both homopolymers and copolymers of propylene are referred to with the term propylene polymer. In particular the suitable propylene polymers are (co)polymers having an isotactic index higher than 0.1%, copolymers comprising one or more alfa-olefins having 2-10 carbon atoms, for example ethylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene; polypropylene compositions obtained

- 7 -

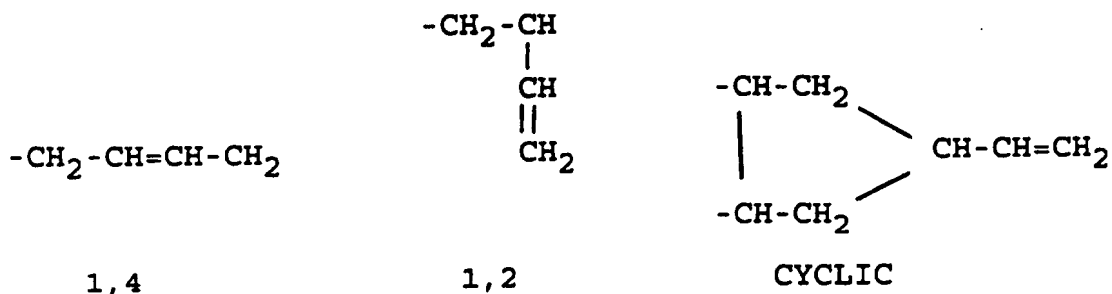
through sequential polymerization of propylene and its mixture with ethylene and/or alfa-olefins; syndiotactic propylene polymers; blends of propylene (co)polymers with EP(D)M (in this latter case the EP(D)M polymers do not act as grafting units).

The propylene (co)polymers have a Melt-Flow-Index (MFI) comprised in the range from 0.1 to 1000 g/10 min, preferably between 0.2 and 60 at 230°C/21.6N (according to ASTM 1238). The amount of propylene polymers is usually at least 10% by weight.

The vinyl polybutadienes, i.e. liquid polymers of butadiene, are usually prepared by anionic polymerisation of butadiene using organolithium catalysts in a solvent, e.g. toluene, that is removed at the end of the reaction. Butadiene monomer, the fundamental building unit, has the chemical formula:



The anionic polymerisation of butadiene leads to polymer chains containing structure of three fundamental different types:



- 8 -

Preferably the polybutadiene, herein referred to as vinyl polybutadiene, used has a content of at least 20% of 1,2 structure and the molecular weight (Mn) is within the range from 900 to 10,000.

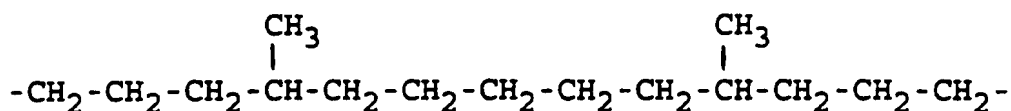
The quantity of vinylbutadiene used in the process of the invention is preferably not greater than 10% by weight, preferably comprised between 0.1 and 5% by weight of the total amount of resin.

The preferred polyalkenylene used is a polyoctenylene, which is produced from cyclo-octene by the so called metathesis polymerisation. It consists of linear as well as cyclic macromolecules which are unbranched and contain one double bond per 8 carbon atoms. The double bonds may be arranged in TRANS or in CIS configuration. The grade of crystallinity depends on the contents of TRANS configuration.

Examples of these polymers are the Vestenamer 8012 and 6213 (TM) commercialised by Hüls AG. The quantity of polyalkenylene used in the process of the invention can vary within a large range; generally the quantity is less than 30% by weight and preferably comprised between 1 and 20% by weight of the total composition.

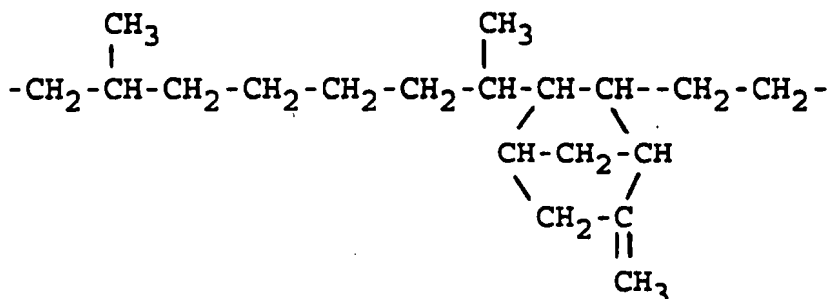
The EPM and EPDM polymers are obtained through copolymerization of ethylene-propylene to give the following base units

- 9 -



EPM copolymer macromolecule

or ethylene-propylene and a not conjugated diene monomer,
to give



EPDM terpolymer macromolecule

Examples of this kind of materials are the Dutral CO and Dutral TER (TM) produced and commercialised by Enichem Elastomeri. EPM and EPDM polymers are used as such, i.e. in a "dry" form, or extended with oils, i.e. after being added with paraffin/naphthene oils to increase their softness. The amount of oil added can reach 90-100% by weight of the EP(D)M polymer. The quantity of EPM or EPDM in the "dry" form is within the range of 5 to 65% by weight, preferably within 5 to 45% and most preferably within 8 to 30% by weight of the total composition. Addition of oil to the EP(D)M polymers results in increased softness and lower costs of the final polymer composition.

- 10 -

The radical initiator can be selected among the peroxide ones as for example dicumyl-peroxide (commercialised as Perkadox BC-FF (TM) by Akzo Nobel, or DCUP (TM) by Peroxid Chemie GmbH), 2,5-bis(tert-butylperoxy)-2,5-dimethyl hexane (commercialised as Trigonox 101 (TM) by Akzo Nobel or DHBP (TM) by Peroxid-Chemie). Among the non-peroxide ones, suitable initiators are those such as 2,3-dimethyl-3,4-diphenyl hexane (commercialised as Perkadox 58 (TM) by Akzo Nobel or CCDFH (TM) by Peroxid-Chemie), 2,3-dimethyl-2,3-diphenyl butane (commercialised as Perkadox 30 (TM) by Akzo Nobel or CCDFB by Peroxyd Chemie).

The contents of radical initiators according to the invention can vary within a wide range according to the required effect, namely within 0.05 to 3.5% by weight preferably from 0.1 to 2.5% by weight of the total composition.

In order to prevent oxidative thermodegradation phenomena during the reactive process, antioxidants and stabilisers are used. Among the primary antioxidants can be mentioned sterically hindered phenols such as 2,6-di-tert-butyl-4-methylphenol (BHT) and secondary amines. Suitable secondary antioxidants are thioethers, phosphites and phosphonites. The antioxidants contents usually is not higher than 1.5% preferably between 0.1 and 1.0% by weight.

- 11 -

The invention will be now further described with reference to the following examples with the aim of illustrating and not limiting the invention.

In the following examples it is used, as reference value for tackiness, the "fogging value" (it means the absence of polymer short chains able to migrate towards surface). The fogging value is expressed as the percent of light transmitted through a glass sheet perfectly transparent, taken as reference, on which the substances that, upon heating, migrate to the surface of the specimen and then to the glass sheet are deposited. The lower is the transmission value the higher is the superficial migration.

EXAMPLES

- EXAMPLE 1

500 parts by weight of polypropylene copolymer with a Melt Flow Index (MFI) of 0.6 dg/min (measured according to ASTM 1238/L), Hardness Shore D of 323 (measured according to ASTM D 2240) and a fogging value of 95% (according to DIN 75201) commercialised by Montell (commercial name (TM) Hifax CA10A) were subjected to mixing with 0.75 parts by weight of antioxidant (Irganox 1035 (TM) produced and commercialised by Ciba-Geigy) and with 1.15 parts of peroxide radical initiator 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane supported on silica (commercial name (TM)

- 12 -

Trigonox 101-50d-pd by Akzo Nobel).

The mixture was fed into the hopper of a twin screws extruder MD30 by Bausano with a thread of 30 mm and a L/D ratio of 19.

The mixture was then extruded operating at a temperature in the screws cylinder between 200 and 220°C with a flow rate of 20 Kg/h, screws speed of 25 rpm and a stay time between 60 and 180 sec. The polymer is extruded in a string shape that afterwards is granulated.

The pellet, so produced, characterized according to ASTM 1238/L (Melt Flow Index) gave a value of 16 dg/min, hardenss Shore D=35 and a fogging value <75% (DIN 75201).

The characterization showed a dramatic decrease of the fogging value, accompanied by an excessive tackiness of the specimen surface.

Both phenomena are due to the polymer chain degradation (molecular weight reduction) because of the use of the radical initiator.

- EXAMPLE 2

Further 1.15 parts by weight of Trigonox 101/50 (TM) are added to the mixture described in example 1. The extrusion and the granulation are perfomed following the example 1. The melt flow index value according to ASTM 1238L is 100 dg/min, hardness Shore D (ASTM D2240) is 38 and the fogging values <70%.

- 13 -

- EXAMPLE 3

5 parts by weight of a liquid vinyl polybutadiene, having an average molecular weight of 2600 and a viscosity at 25°C of 85 Poise (produced and commercialised by Revertex Ltd. as Lithene PH (TM)) were added to the mixture mentioned in the reference example 2.

The pellets production was performed according to example 1. The melt flow index became 20 dg/min, the hardness Shore D=35 and the fogging values less than 85%.

- EXAMPLE 4

15 parts by weight of a polyalkenylene (produced and commercialised by Hüls AG as Vestenamer 8012 (TM)) are added to the mixture of example 3. The extrusion and the pellets production were performed according to example 1. The characterization values are as follow:

- MFI = 13 dg/min;
- hardness Shore D = 25;
- fogging >93%.

- EXAMPLE 5

25 parts by weight of Vestenamer 8012 (TM) were added to the mixture of example 2. The pellets production was performed according to example 1.

The characterization values were as follows :

- MFI = 16 dg/min;
- hardness Shore D = 25;

- 14 -

- fogging >95%.

- EXAMPLE 6

225 parts by weight of a polypropylene copolymer with a melt flow rate 230°C/2.16N of 45 g/10min (according to ISO 1133), flexural modulus of 1350 MPa (according to DIN 53457) and fogging value >95% produced and commercialised by PCD polymers as USC 1012A were subjected to mixing with 270 parts by weight of an amorphous ethylene-propylene copolymer (EPM) with an extended oil content of 50% by weight with a Mooney viscosity ML(1+4) at 125°C of 31, produced and commercialised by Enichem Elastomeri as Dutral CO 554 (TM), and with 0.75 parts by weight of a phenolic antioxidant (Irganox 1035, TM, produced and commercialised by Ciba-Geigy) and 0.75 parts by weight of a peroxide radical initiator, DHBP-45 IC/G 2,5-Dimethyl-2,5 di(terbutyl peroxy) hexane (45% by weight with chalk) produced and commercialised by Peroxid Chemie GmbH.

The mixture was then extruded operating at a temperature in the screws cylinder between 170°C and 210°C, with a flow rate of 40 Kg/h, screw speed of 20 rpm and a stay time between 60 and 180 sec.

The polymer is extruded in a string shape and granulated. The pellets, so produced, characterized according to ASTM 1238/L (melt flow index) gave a value of 34 dg/min and fogging value >95% (DIN 75201).

- 15 -

- EXAMPLE 7

167.5 parts by weight of a polypropylene copolymer USC 1012A were subjected to mixing with 332.5 parts by weight of Dutral CO 554, with 0.75 parts by weight of Irganox and 1.75 parts by weight of DHBP-45 IC/G.

The pellet production was performed according to example 6. The characterization values are as follows :

- MFI = 31 dg/min;
- hardness Shore D = 68;
- fogging >95%.

- EXAMPLE 8

164.5 parts of a propylene copolymer USC 1012A were subjected to mixing with 325.5 parts by weight of Dutral CO554, 10 parts by weight of vinyl polybutadiene (Lithene PH (TM) by Revertex Ltd.) and 1.75 parts by weight of DHBP-46 IC/G. The pellet production was performed according to example 6. The obtained characterization values are as folllows :

- MFI = 18.5 dg/min
- hardness Shore A = 68
- fogging >90%.

- 16 -

CLAIMS

1. Propylene homo and copolymers comprising grafting units, characterized in that said grafting units are selected from polyalkenylenes, EPM and EPDM polymers, or mixtures thereof, the amount of polyalkenylenes being within the range from 1 to 30% by weight and the amount of EPM and/or EPDM polymers being within the range from 5 to 65% by weight of the total composition weight.
2. Propylene homo and copolymers according to claim 1, further comprising vinylpolybutadienes as grafting units, the amount of vinylpolybutadiene being within the range from 0.01 to 10% by weight.
3. Propylene homo and copolymers according to claim 1 or 2, wherein said EPM and/or EPDM polymers are extended with an additional amount of oil, said additional amount of oil being within the range from 1 to 60% by weight of the amount of EPM/EPDM polymers.
4. Propylene homo and copolymers according to claim 1, 2 or 3, comprising vinyl polybutadienes within a range from 0.1 to 5.0% by weight and polyalkenylenes within a range from 1.5 to 20% by weight.
5. Propylene homo and copolymers according to any previous claim, wherein said vinylbutadiene comprises at least 20% of 1,2 structures.
6. Propylene homo and copolymers according to any previous

- 17 -

claim, wherein said polyalkenylene is polyoctenylene.

7. Propylene homo and copolymers according to any previous claim, wherein the starting propylene (co)polymers are ethylene-propylene copolymers.

8. A process of producing grafted propylene homo and copolymers by selective degradation in the presence of radical initiators and grafting units, characterized in using grafting units selected from polyalkenylenes, EPM and EPDM polymers, or mixtures thereof, the amount of polyalkenylenes being within the range from 1 to 30% by weight and the amount of EPM and/or EPDM polymers being within the range from 5 to 65% by weight of the total composition weight.

9. A process according to claim 8, wherein vinyl polybutadienes are also used as grafting units in an amount within the range from 0.01 to 10% by weight.

10. A process according to claim 8 or 9, wherein said EPM and/or EPDM polymers are extended with an additional amount of oil, said additional amount of oil being within the range from 1 to 60% by weight of the amount of EPM/EPDM polymers.

11. A process according to any claim 8 to 10, wherein vinyl polybutadiene within a range from 0.1 to 5.0% by weight and polyalkenylenes within a range from 1.5 to 20% by weight are used as grafting units.

- 18 -

12. A process according to any claim from 8 to 11, wherein said vinyl polybutadiene comprises at least 20% of 1,2 structures and/or said polyalkenylene is polyoctenylene.

13. A process according to any claim 8 to 12, wherein said radical initiators are peroxide radical initiators.

14. A blend for producing grafted propylene homo and copolymers having a composition according to any claim 1 to 7.

15. The use of propylene homo and copolymers according to any claim 1 to 7 as the outer skin material in the production of interior car door panels or car trim elements.

16. An interior car door panel or car trim element characterized in that it has an outer skin made of propylene homo and copolymers according to any claim 1 to 7.

17. An interior car door panel or car trim element according to claim 16, characterized in being obtained by coinjection molding.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L23/10 C08L23/16 C08L65/00 //(C08L23/10,65:00),
 (C08L23/10,23:16),(C08L23/16,23:10),(C08L65/00,23:10),(C08L65/00,
 23:16)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L B29C B60R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	US,A,5 503 923 (GOTO MASAOMI ET AL) 2 April 1996	15-17
A	& DATABASE WPI Derwent Publications Ltd., London, GB; AN 95-018824 & JP,A,06 305 080 (TOYODA) , 1 November 1994 see abstract	15-17
Y	EP,A,0 546 289 (COMMER SPA) 16 June 1993 see column 2, line 36 - line 51	15-17
X	EP,A,0 618 259 (MITSUI TOATSU CHEMICALS) 5 October 1994	1,3,8, 10,15,16
Y	see page 2, line 47 - page 5, line 48	15-17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 May 1996

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 376 213 (SHOWA DENKO KK) 4 July 1990 see page 2, line 5 - line 20 see page 2, line 52 - page 3, line 55 see page 4, line 55 - page 5, line 34 see page 6, line 30 - line 35 ---	1,3,8,10
X	EP,A,0 542 253 (SVILUPPO SETTORI IMPIEGO S R L ;SVILUPPO SETTORI IMPIEGO SRL (IT)) 19 May 1993 cited in the application see page 2, line 31 - page 3, line 3 ---	4,5,9, 11,12
X	FR,A,2 527 217 (FREUDENBERG CARL) 25 November 1983 see page 5, line 1 - line 6 see examples 3,5 ---	1,2,7-9, 13,14
X	EP,A,0 428 153 (HIMONT INC) 22 May 1991 ---	1,2,7-9, 13,14
Y	see page 2, line 48 - page 3, line 26 ---	4,11,12
X	EP,A,0 624 622 (SPHERILENE SRL) 17 November 1994 cited in the application see page 2, line 35 - page 3, line 54 -----	1,6-8, 12-14
Y		4,11,12

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5503923	02-04-96	JP-A-	6305080	01-11-94
		JP-A-	6305081	01-11-94
		JP-A-	6328508	29-11-94

EP-A-0546289	16-06-93	IT-B-	1252239	05-06-95
		JP-A-	5229035	07-09-93

EP-A-0618259	05-10-94	JP-A-	6287368	11-10-94

EP-A-0376213	04-07-90	JP-A-	3064341	19-03-91
		JP-A-	2170845	02-07-90
		DE-D-	68913482	07-04-94
		DE-T-	68913482	01-09-94
		US-A-	4985502	15-01-91

EP-A-0542253	19-05-93	IT-B-	1252388	12-06-95
		JP-A-	6041251	15-02-94

FR-A-2527217	25-11-83	DE-C-	3219331	29-12-83
		GB-A-	2123004	25-01-84
		SE-A-	8300024	23-11-83

EP-A-0428153	22-05-91	US-A-	4948840	14-08-90
		AT-T-	120221	15-04-95
		AU-B-	642441	21-10-93
		AU-B-	6659490	23-05-91
		CA-A-	2028025	15-05-91
		CN-A-	1051740	29-05-91
		DE-D-	69018015	27-04-95
		DE-T-	69018015	26-10-95
		JP-A-	3168235	22-07-91

EP-A-0624622	17-11-94	JP-A-	7002956	06-01-95
		US-A-	5480942	02-01-96
